EFFECT OF EXTRUSION COOKING AND SODIUM BICARBONATE ADDITION ON THE CARBOHYDRATE COMPOSITION OF BLACK BEAN FLOURS

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ABSTRACT

*Extrusion cooking and chemical leavening agents such as sodium bicarbonate ($NaHCO_3$), may induce changes in carbohydrate fractions of extruded black bean (*Phaseolus vulgaris* L.) flours. Bean flours at 20% moisture, with $NaHCO_3$ added at levels from 0.0 to 2.0%, were extruded at a screw speed of 200 rpm. The temperature profile ranged from 23 to 160C. Extruded bean flours with 0.1 to 0.4% added $NaHCO_3$ were selected for sugar analyses based on color and flavor acceptability. The major sugars determined in the bean samples were galactose (0.10%), sucrose (2.08%), and stachyose (2.00%). Extruded samples had an increase in total sugars. Also, an increase in soluble fiber and a decrease of insoluble fiber fractions were observed. Sucrose was the only free sugar which concentration decreased consistently as a result of extrusion processing. Extrusion conditions and the selected levels of $NaHCO_3$ used in this study did not significantly change the oligosaccharide content of the black bean flours.*

INTRODUCTION

Extrusion cooking technology is considered a high-temperature-short-time, versatile, and modern food operation. Cooking of foods at high temperatures,

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in a matter of seconds, generally has favorable effects in maintaining the properties of food components and active ingredients, while drastically reducing or completely eliminating microorganisms present in starting materials. Therefore, the final extruded food product, having low moisture content, is considered a shelf-stable product.

The most common processing steps in the extruder-cooker are gelatinizing, dissolving, denaturing, roasting, mixing, shaping, and expanding (Wiedman and Strobel 1987). Due to the processing flexibility offered by extrusion cooking technology, extrusion cooking has found important uses in the cereal and pet food industries, as well as in dairy, bakery, beverage and confections industries. Drum dryers, cooking vessels, and stirred reactors are among the main processing equipment that can sometimes be replaced by a single extrusion unit.

Consumers find expanded, ready-to-eat extruded snack products very attractive because of convenience, textural attributes, shelf stability, and enhanced flavor. Additionally, the nutritional appeal of high-protein, high-nutritional, low-caloric snacks is a value-added attribute of extruded products from plant origins such as legume seeds. Industrial production of snack foods from plant proteins has grown rapidly since the 1970's resulting from interest of food manufacturers to produce a wide range of high-protein food products, using different sources of plant protein (Skierkowski *et al.* 1990).

Dry bean (*Phaseolus vulgaris* L.) is a legume and is a rich source of protein, carbohydrates, dietary fiber, vitamins, and minerals. However, the presence of sugars (particularly oligosaccharides of the raffinose family) that cause flatulence in man and animals, reduce the acceptability of dry bean products (Calloway *et al.* 1971; Fleming 1981; Abdel-Gaward 1993). Baking soda or sodium bicarbonate ($NaHCO_3$) is a leavening agent that has been widely used in the bakery industry and more recently used in directly expanded extruded cereal products to enhance their physical properties (Lai *et al.* 1989; Lajoie *et al.* 1996; Parsons *et al.* 1996). The desirable influence of $NaHCO_3$ on flavor ("honey-toasted") and color ("browning") are a consequence of Maillard and caramelization reactions, both of which are enhanced at high pH and temperature (Ellis 1959; Whistler and Daniel 1985). While the effects of $NaHCO_3$ on extruded cereal products have been studied, its effects on extruded bean flours have not been examined.

Extrusion of bean flour under high pH, temperature, and pressure may induce desirable chemical and physical changes in the extruded product. The purpose of the present study was to evaluate the changes in carbohydrate composition of black bean flours extruded in the presence of various $NaHCO_3$ concentrations.

MATERIALS AND METHODS

Extrusion Material

Commercial black beans (*Phaseolus vulgaris* L.) grown in California were obtained from Giusto's Specialty Foods, Inc. (So. San Francisco, CA). The beans were blended in a paddle type mixer (Marion Mixer, Rapid Machinery Co., Marion, IA) to a uniform lot. Beans were then ground in a disc attrition mill (CE-Bouer, Springfield, OH) equipped with a Dayton AC inverter model No. 1XC98A (Dayton Electric Mfg. Co., IL) operated at 3,600 rpm, using 8118 plates for the production of bean flours.

Black bean flours were mixed in different proportions with certified A.C.S. $NaHCO_3$ powder (Fisher Scientific, Fair Lawn, NJ) in a Hobart mixer (Model A-200, The Hobart Mfg. Co., Troy, OH) for 5 min at speed 1, to give flours containing 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0 and 2.0% of $NaHCO_3$. The mixtures were extruded at moisture content of 20% (wwb) by adjusting the amount of water in the extruder.

Extrusion Conditions

A Leistritz Micro-18-GL twin-screw extruder (American Leistritz Extruder Corp., Sommerville, NJ) equipped with a 5-hp motor and corotating intermeshing screws, containing three pairs of right handed kneading blocks (Fig. 1) was used at a constant screw speed of 200 rpm. Five of the six extruder-barrel sections were electrically heated and air-cooled. The first barrel section (feed section) was water-cooled. The temperature profile selected for this study was 23, 80, 100, 120, 140, and 160C with the first temperature corresponding to the feed barrel section and the last to the die section. Barrel sections had a L:D ratio of 5:1. The die consisted of two circular openings 2 mm in diameter. Bean flour was metered into the feed section by a twin-screw, loss-in-weight gravimetric feeder (Model KCL 24-T20, K-Tron Corp., Pitman, NJ) at 80 g/min regulated by a K-Tron Series 6300 digital speed controller. Water was metered into the second barrel section by a variable stroke piston pump (Model N-P 32, Bran and Luebbe, Buffalo Grove, IL) to adjust the moisture content of the bean flour undergoing extrusion to 20% (wwb). Extruded bean material was collected for 6 min, approximately 10 min after the operation conditions of torque and pressure reached steady state.

Extrudate Collection

Extruded bean material was collected in stainless steel trays, cooled down to room temperature, bagged in zip-lock plastic bags, and stored at refrigeration temperature.

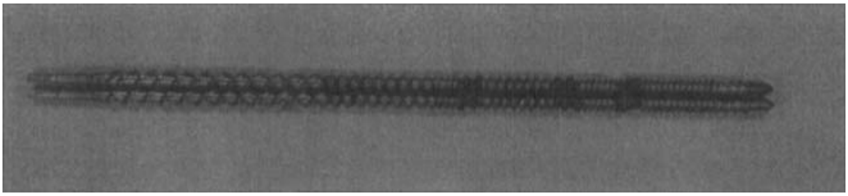

FIG. 1. EXTRUDER SHAFT WITH COROTATING INTERMESHING SCREWS AND THREE PAIRS OF RIGHT-HANDED KNEADING BLOCKS

Analysis

Bean Flours. Bean flours were obtained by grinding nonextruded and extruded bean materials in a Udy mill (Udy Corp., Fort Collins, CO) through a 0.5 mm screen. The bean flours were used for all subsequent analyses.

Proximate Analysis. Proximate analysis on the raw bean flour was performed in duplicate and reported on a dry weight basis. Moisture content was determined by standard AACC (1984) method 44-15, and ash, using standard AOAC (1990) method 923.03. Crude fat was determined by weight difference after sample extraction with certified A.C.S. petroleum ether (Fisher Scientific, Fair Lawn, NJ) in an Accelerated Solvent Extractor (ASE) 200 (Dionex Corp., Sunnyvale, CA). The ASE extraction conditions used in this study were: temperature, 125C; pressure, 1000 psi; heat-up time, 6 min; static time, 25 min; flush volume, 60%; purge time, 90 s; static cycles, 1. Total nitrogen was determined by combustion using a FP-428 nitrogen analyzer (Leco Corp., St. Joseph, MI), and the crude protein content was calculated, using a factor of 6.25. Total carbohydrates were calculated by difference.

pH Measurement. pH measurement was determined in triplicate on 1 g of flour slurried in 20 mL distilled water, using a Beckman ϕ 45 pH meter (Beckman Instruments, Fullerton, CA).

Total Available Carbohydrates. Total available carbohydrates content was evaluated after acid hydrolysis by a colorimetric method using anthrone color reagent (Osborne and Voogt 1986).

Oligosaccharides. Oligosaccharides were analyzed by HPLC after ethanol extraction as described by Sanchez-Mata *et al.* (1998).

Insoluble Fiber. Insoluble fiber was determined by an enzymatic-gravimetric method, using α-amylase for starch hydrolysis (AACC 1984).

Soluble Fiber. Soluble fiber was determined as total uronic acids in the alcohol soluble and insoluble residues as described by Blumenkrantz and Asboe-Hansen (1973), and Ahmed and Labavitch (1977), respectively.

Instrumentation

A Waters Associates liquid chromatograph (Milford, MA) equipped with a 6000A pump, a U6K injector, and a differential refractometer R401 was used. The column used was a Waters μBondapak/carbohydrate analysis column. The mobile phase was acetonitrile:water (80:20) run at a flow rate of 0.9 mL/min at ambient temperature. All chromatograms were recorded on a Waters Data Module 745 integrator.

Statistical Analysis

The multifactorial analysis of variance was applied to determine significant main effects (extrusion process and $NaHCO_3$ addition) and interactions at 95% confidence interval. The statistical analysis was done on duplicated samples using the program Statgraphics Plus 4.1 for Windows.

RESULTS AND DISCUSSION

Proximate analysis showed that the black bean flour used in this study contained 9.83% moisture, 24.68% crude protein, 2.25% crude fat, 4.30% ash, and 58.94% total carbohydrates (calculated by difference). These values were similar to those reported for black bean flours by Koehler *et al.* (1987) and Berrios *et al.* (1999). Dry bean flours have been reported to contain 44.43 (Jood *et al.* 1986) and 37.9% (Marconi *et al.* 2000) starch. This indicates that total carbohydrate in dry bean flours is composed mainly of starch.

Figure 2 shows the extruded bean rods with and without (control) $NaHCO_3$ addition. Sodium bicarbonate had a direct effect on both expansion and color of the extruded bean rods as a consequence of $NaHCO_3$ capacity for acting as a leavening agent and as an alkaline agent, respectively. As observed, the extruded bean rods increased in expansion and brown color with an increase in $NaHCO_3$ addition. Greater expansion of extruded bean rods was considered a desirable attribute of $NaHCO_3$ addition, while excessive browning was considered undesirable. Chiang and Johnson (1977) reported that the 2→1-furanosidic bonds in sucrose and raffinose could be broken during extrusion cooking and that extrusion conditions influenced the extent of this result. The nonreducing sugar sucrose, released through this reaction, is converted to reducing monosaccharides capable of participating in the Maillard reaction. Additionally, high pH and temperature enhance the Maillard reaction (Ellis 1959; Whistler and Daniel

1985). The increased browning observed in the extruded bean samples with an increase in $NaHCO_3$, indicates that the $NaHCO_3$ addition and high processing temperature used in this study favored the Maillard reaction.

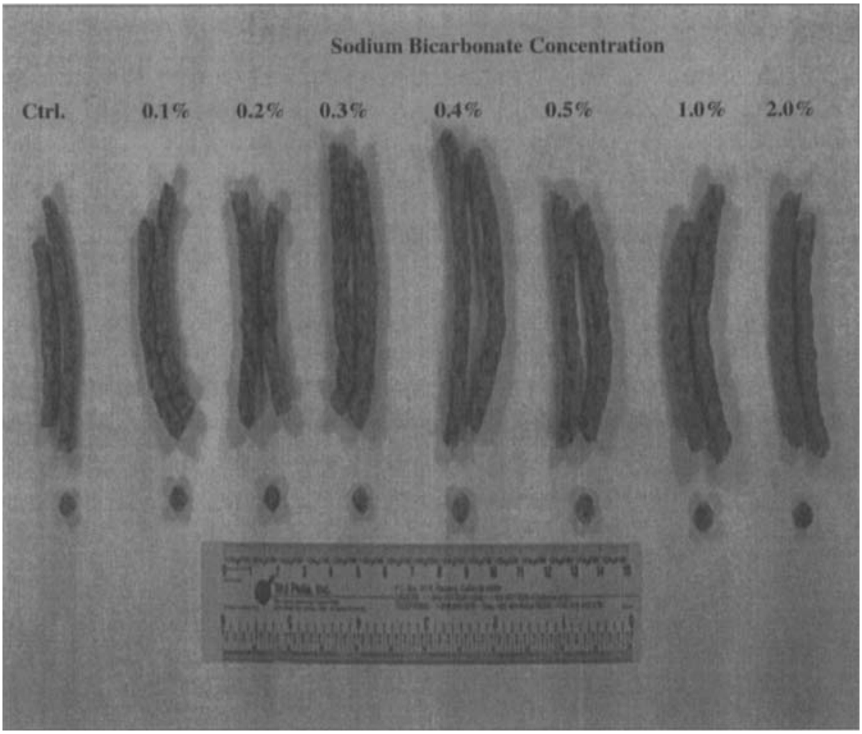

FIG. 2. EXTRUDED BLACK BEAN RODS WITH VARIOUS LEVELS OF SODIUM BICARBONATE ADDITION

Sugars, oligosaccharides, and soluble and insoluble fibers were determined only on nonextruded and extruded bean flours having up to 0.4% added $NaHCO_3$. The selection of these samples was made based on color and flavor acceptability of the extruded bean products. Extruded bean products with 0.5, 1.0, and 2.0% added $NaHCO_3$, visually showed pronounced browning color compared to the control-extruded products and extruded bean products with lower $NaHCO_3$ concentrations (Fig. 2). Additionally, extruded bean products having 1.0 and 2.0% added $NaHCO_3$ had a soapy taste and were, therefore, considered unacceptable for consumption. Based on the stated color and flavor considerations, these samples were excluded from the study.

The pH values of nonextruded and extruded bean flours (Table 1) increased with increased $NaHCO_3$ concentration. Also, extruded bean flours demonstrated higher pH values than nonextruded bean flours. The increase in pH values was probably due to a more effective alkaline action of the $NaHCO_3$ in the extruded bean flours resulting from the combined effect of multiple extrusion processing operations such as mixing, kneading, shearing, cutting, and cooking, among others. These combined processing operations may have promoted chemical reactions between $NaHCO_3$ and macromolecules in the bean flours, particularly protein and starch that represent the largest portion of the components in dry beans, which modified the pH of the flours.

TABLE 1.
pH VALUES OF NONEXTRUDED AND EXTRUDED BEAN SAMPLES[1]

% $NaHCO_3$ Addition	Non-Extruded pH	Extruded pH
0	6.42 ± 0.01	6.60 ± 0.01
0.1	6.52 ± 0.01	6.63 ± 0.02
0.2	6.63 ± 0.01	6.70 ± 0.01
0.3	6.70 ± 0.01	6.80 ± 0.01
0.4	6.76 ± 0.01	7.02 ± 0.01

[1]pH values were determined on flour to water ratio of 1:25.

Table 2 shows the carbohydrate composition of nonextruded and extruded bean samples represented by their mean values and their corresponding standard deviations. Total sugars (TS) were the major component determined, followed by insoluble fiber (IF) and total uronic acids as a measurement of soluble fiber (SF). Comparing the carbohydrate composition of nonextruded versus extruded samples, it was determined that nonextruded samples demonstrated lower concentrations of TS, free sugars, and SF, and higher concentrations of IF than extruded samples. A notable exception, which we cannot explain, was TS at 0.1% $NaHCO_3$ addition, where the average value of the nonextruded samples was higher than the average value of the extruded samples. Moreover, the data showed that the values of the nonextruded samples, as well as those of the extruded samples, varied among the different levels of $NaHCO_3$ addition. Results obtained by the multifactor analysis of variance (Table 4) that measured the significant variability ($P<0.05$) of carbohydrate composition resulting from extrusion processing, $NaHCO_3$ addition, and/or their interaction, confirmed this observation. In general, the statistical results indicate that $NaHCO_3$ addition was

TABLE 2.
CARBOHYDRATE COMPOSITION OF NONEXTRUDED AND EXTRUDED BEAN SAMPLES (G/100G WWB)

Addition	Process	Moisture	Total Sugars	Free Sugars	Insoluble Fiber	Soluble Fiber
0.0% $NaHCO_3$	Non-Extruded	9.83±0.02	34.56±1.35	4.14±0.41	11.73±0.79	6.02±0.18
(Control)	Extruded	9.50±0.01	38.56±0.57	4.48±0.75	10.61±0.26	6.91±0.05
0.1% $NaHCO_3$	Non-Extruded	10.16±0.01	37.18±1.16	2.27±0.16	11.41±0.43	5.46±0.09
	Extruded	9.83±0.00	33.31±0.95	5.20±0.18	9.08±0.57	5.21±0.07
0.2% $NaHCO_3$	Non-Extruded	10.08±0.04	38.89±1.68	3.98±0.51	12.42±0.87	4.93±0.02
	Extruded	9.89±0.06	41.94±1.87	5.12±0.62	8.88±0.73	7.84±0.14
0.3% $NaHCO_3$	Non-Extruded	10.30±0.02	32.63±0.44	4.42±0.14	9.29±0.81	3.99±0.04
	Extruded	10.55±0.01	39.49±0.09	4.66±0.03	8.06±0.82	5.48±0.41
0.4% $NaHCO_3$	Non-Extruded	10.27±0.02	32.63±0.82	4.24±0.06	11.26±0.20	5.09±0.24
	Extruded	10.44±0.02	39.14±1.01	4.95±0.18	8.77±0.68	6.10±0.29

the parameter that induced the major source of significant variation in the carbohydrate components analyzed in this study.

To our knowledge, increase in total and free sugar content in beans or other seeds resulting from extrusion processing have not been previously reported. On the other hand, the observed decrease in IF and increase in SF confirms that extrusion processing causes a redistribution of the IF to SF fractions as it has been previously reported by other researchers (Björck *et al.* 1984; Lintas *et al.* 1995; Gualberto *et al.* 1997). This fiber fraction redistribution possibly resulted from hemicellulose depolymerization. Other authors, however, did not observe changes in fiber modification resulting from extrusion processing (Artz *et al.* 1990).

To illustrate the free sugar profile determined in this study, the HPLC chromatograms of free sugars in nonextruded and extruded bean control samples, and bean samples with 0.4% $NaHCO_3$ addition (Fig. 3), were selected. The identified and quantified monosaccharides: glucose, galactose, and myoinositol; disaccharides: sucrose and maltose; oligosaccharides: raffinose and stachyose are shown with their respective elution times. The different sugars were determined by comparing HPLC sugar profiles of the bean samples with commercial sugar standards. The presence of the monosaccharide glucose that eluted just before galactose was usually undetectable (Fig. 3) in the bean flour samples. Sanchez-Mata *et al.* (1998) were unable to detect glucose in white and pinto beans and found only trace levels of this sugar in lentils. Maltose and myoinositol eluted at the same retention time, therefore their concentrations were quantified together in Table 3.

The pentasaccharide verbascose, is a nondigestible oligosaccharide present in a variety of legume seeds including lupine, chick pea, field pea, mung bean (Sosulski *et al.* 1982), lima bean (Meredith *et al.* 1988), faba bean, lentil, and cowpea (Abdel-Gaward 1993). It is also present in the seed of some dry bean cultivars such as navy bean (Sosulski *et al.* 1982) and red bean (Ruperez 1998). However, verbascose was not detected in any of the black bean flour samples analyzed in the present study. Other authors have reported its absence in white kidney and pinto bean samples (Phillips and Abbey 1989; Sanchez-Mata *et al.* 1998). This indicates that the presence or absence of this pentasaccharide in different legume cultivars may be genotype specific.

Table 3 shows the free sugars composition determined in nonextruded and extruded bean samples. The major monosaccharide, disaccharide, and oligosaccharide present in the bean samples were galactose, sucrose, and stachyose, respectively. Values obtained for galactose (0.01-0.10%) and sucrose (1.45-2.08%) in this study were similar to those obtained by Sanchez-Mata *et al.* (1998) in white and pinto beans. Values for the combined sugars maltose and inositol (0.21-0.42%) in beans or other grains have not been previously reported.

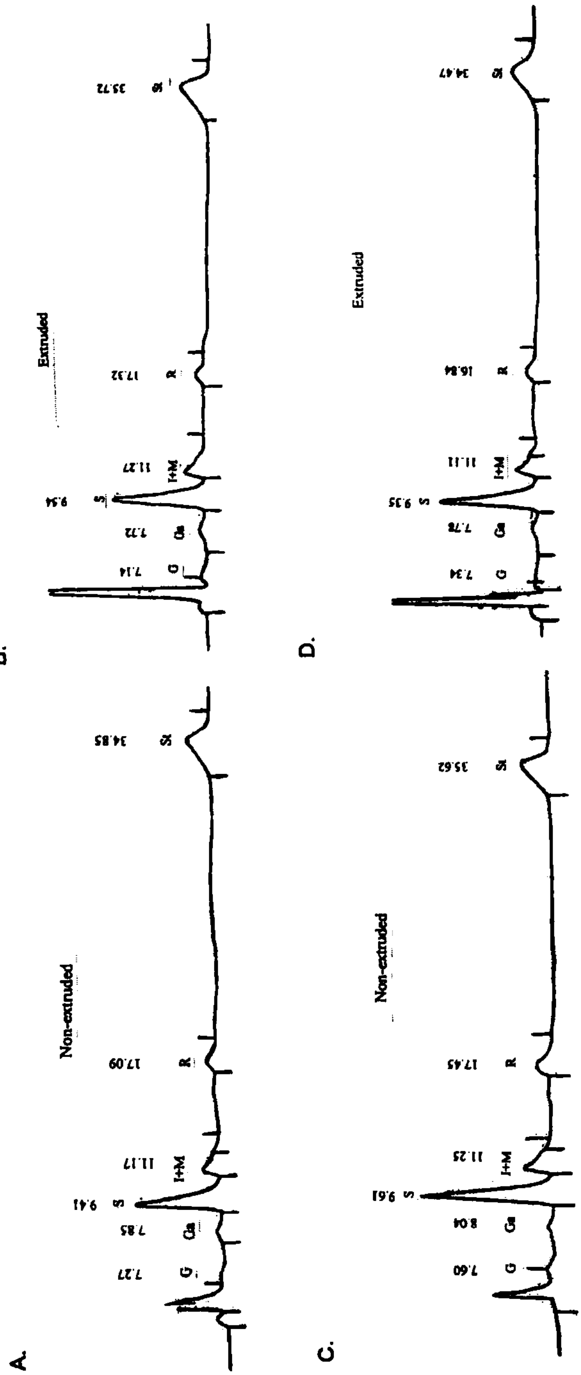

FIG. 3. HPLC PROFILE OF FREE SUGARS IN CONTROL[1] BEAN FLOURS AND BEAN FLOURS WITH 0.4% $NAHCO_3$ ADDITION[2]
(G: GLUCOSE, GA: GALACTOSE, S: SUCROSE, I: INOSITOL, M: MALTOSE, R: RAFFINOSE, ST: STACHYOSE)
[1]A: free sugars in nonextruded control bean flours; [1]B: free sugars in extruded control bean flours.
[2]C: free sugars in nonextruded bean flours with 0.4% $NaHCO_3$; [2]D: free sugars in extruded bean flours with 0.4% $NaHCO_3$.

TABLE 3.
COMPOSITION OF FREE SUGARS IN NONEXTRUDED AND EXTRUDED BEAN SAMPLES (G/100G WWB)

Addition	Process	Glucose	Galactose	Sucrose	Maltose + Inositol	Raffinose	Stachyose
0.0% $NaHCO_3$	Non-Extruded	0.00±0.00	0.01±0.01	2.08±0.05	0.35±0.28	0.35±0.04	1.41±0.12
	Extruded	0.01±0.00	0.05±0.01	2.01±0.02	0.42±0.24	0.47±0.04	1.78±0.03
0.1% $NaHCO_3$	Non-Extruded	0.00±0.00	0.05±0.01	1.77±0.04	0.24±0.03	0.24±0.05	1.01±0.04
	Extruded	0.03±0.01	0.03±0.01	1.58±0.05	0.24±0.19	0.27±0.01	1.33±0.08
0.2% $NaHCO_3$	Non-Extruded	0.00±0.00	0.06±0.00	1.99±0.03	0.30±0.02	0.31±0.09	2.00±0.08
	Extruded	0.00±0.00	0.02±0.01	1.71±0.01	0.21±0.01	0.27±0.02	1.34±0.04
0.3% $NaHCO_3$	Non-Extruded	0.04±0.01	0.04±0.01	1.68±0.14	0.21±0.05	0.20±0.04	0.98±0.06
	Extruded	0.00±0.00	0.08±0.01	1.45±0.04	0.25±0.01	0.27±0.03	1.54±0.04
0.4% $NaHCO_3$	Non-Extruded	0.00±0.00	0.06±0.01	1.92±0.10	0.40±0.02	0.19±0.06	1.44±0.06
	Extruded	0.00±0.00	0.10±0.01	1.63±0.10	0.35±0.11	0.21±0.00	1.31±0.04

The oligosaccharides raffinose and stachyose are, from a physiological point of view, the most interesting group of the soluble sugar fraction of legumes because of their role in the formation of gas (flatulence) in the large intestine of humans and monogastric animals. Stachyose content was higher than raffinose in all bean samples, as previously reported for leguminous seeds (Rossi *et al.* 1984; Kuo *et al.* 1988). However, the values of stachyose, which in this study ranged from 1.01-2.00%, are lower than those reported by Olson *et al.* (1981) of 2.9-3.8% and Reddy *et al.* (1984) of 2.4-4.0% in several dry bean cultivars. Borejszo and Khan (1992) reported that raffinose and stachyose contents in the high starch fraction of pinto bean were reduced 47-60% by extrusion processing. However, raffinose and stachyose contents were not reduced under the extrusion conditions used in this study. Processing conditions of moisture and temperature of the two studies were similar. However, Borejszo and Khan (1992) used a larger, more powerful extruder (52 mm, 30 hp), and higher screw speed (300 rpm) than the one used in the present study. Additionally, the high starch fraction of bean used in their study did not contain any insoluble fibrous material, which is concentrated in the bean's seed coat. Power input and screw speed have a direct effect on the shear imparted to the material during extrusion. In the present study, the possible low shearing action on the black bean flours resulting from lower power and screw speed may have limited the fractionation of the oligosaccharides. Furthermore, fibrous seed coat material may prevent oligosaccharides and other sugars from breaking down during extrusion. Studies need to be done to investigate the validity of these statements.

In general, the amount of galactose, maltose-inositol, raffinose, and stachyose varied randomly among the control, nonextruded, and extruded bean samples with added $NaHCO_3$ (Table 3). This tends to indicate that neither the $NaHCO_3$ addition nor the extrusion processing affected the concentration of these sugars. Sucrose was the only free sugar which concentration decreased consistently as a result of extrusion processing. Reduction of sucrose as a result of extrusion processing has also been reported by other authors (Borejszo and Khan 1992). Additionally, the difference in sucrose concentration between the nonextruded and extruded bean samples increased with an increase in $NaHCO_3$ addition. Sucrose forms salts (saccharates) with alkaline compounds (Dè Gruyter 1988). The possible formation of more saccharates in the extruded bean samples, due to mixing and other extrusion processing conditions, than in the nonextruded bean samples may be responsible for the observed reduction in sucrose concentration with an increase in $NaHCO_3$ addition. Table 4 shows that, with the exception of stachyose, the individual free sugars studied were not significantly affected by the source of variation (process, $NaHCO_3$ addition, and their interaction) evaluated here.

TABLE 4.
THE EFFECT OF EXTRUSION PROCESSING, SODIUM BICARBONATE ADDITION, AND THEIR INTERACTIONS ON THE VARIABILITY OF TOTAL AND FREE SUGARS, INSOLUBLE AND SOLUBLE FIBER CONCENTRATION

Source of variation		Total sugars	Free sugars	Insoluble Fiber	Soluble Fiber
Process	F-ratio	**70.2990**	0.4620	**155.6820**	0.1770
	Sig. level	*0.0001*	*0.5194*	*0.0001*	*0.6870*
Addition	F-ratio	**27.0610**	**6.7210**	**13.7210**	**56.3940**
	Sig. level	*0.0001*	*0.0068*	*0.0005*	*0.0001*
Process x Addition interaction	F-ratio	**32.1870**	3.4690	**6.9250**	**82.4310**
	Sig. level	*0.0001*	*0.0501*	*0.0061*	*0.0001*

		Glucose	Galactose	Sucrose	Maltose + Myoinositol	Raffinose	Stachyose
Process	F-ratio	0.0001	0.1960	0.7570	0.0080	0.3870	1.1130
	Sig. level	*0.9899*	*0.6722*	*0.4137*	*0.9335*	*0.5541*	*0.3162*
Addition	F-ratio	0.6660	0.3950	2.1200	1.2010	1.3600	**3.7870**
	Sig. level	*0.6301*	*0.8080*	*0.1529*	*0.3690*	*0.3146*	*0.0399*
Process x Addition interaction	F-ratio	1.2500	0.5570	0.8510	0.1980	0.1840	**5.0740**
	Sig. level	*0.3512*	*0.6993*	*0.5248*	*0.9340*	*0.9415*	*0.0170*

Numbers in bold phase are significantly different ($P \leq 0.05$).

A new study is underway using a larger and more powerful extruder. High screw speeds and temperature, and variable moisture contents are being tested to determine the effect of these variables on the carbohydrate composition of whole bean flours, particularly their effects on reducing the concentration of the oligosaccharides raffinose and stachyose.

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